



Cobalt porphyrin-based material as methanol tolerant cathode in single chamber microbial fuel cells (SCMFCs)

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HIGHLIGHTS

- SCMFCs achieved 100% methanol removal and high COD removal efficiency.
- CoTTP cathodes had high tolerance to methanol than Pt cathodes.
- Methanol can be partly converted to electricity in SCMFCs.
- SCMFCs with CoTTP cathodes had more stable power generation than Pt cathodes.

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ABSTRACT

This study focused on the development of novel cathode material based on the pyrolysis of [*meso*-tetrakis(2-thienyl)porphyrinato]Co(II) (CoTTP) for use in single chamber microbial fuel cells (SCMFCs) to treat wastewater containing methanol. The cathodes produced at two loadings (0.5 and 1.0 mg cm⁻²) were examined in batch mode SCMFCs treating methanol of different concentrations (ranging from 0.005 to 0.04 M) over a 900 h operational period. Methanol was completely removed in SCMFCs, and the cycle duration was prolonged at high methanol concentrations, indicating methanol was used as fuel in SCMFCs. Methanol had more poisoning effects to the traditional platinum (Pt) cathodes than to the CoTTP cathodes. Specifically, power generations from SCMFCs with Pt cathodes gradually decreased over time, while the ones with CoTTP cathodes remained stable, even at the highest methanol concentration (0.04 M). Cathode linear sweep voltammetry (LSVs) indicated that the electrocatalytic activity of the Pt cathode was suppressed by methanol. Higher CoTTP loadings had similar open circuit potential (OCP) but higher electrocatalytic activity than lower loadings. This study demonstrated that methanol can be co-digested with wastewater and converted to power in MFCs, and a novel cathode CoTTP catalyst exhibits higher tolerance towards methanol compared with traditional Pt catalyst.

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1. Introduction

A microbial fuel cell (MFC) is a bio-electrochemical system capable of converting organic substances to electricity [1–8]. The anode of MFC contains supporting media for electrogenic bacteria to grow, degrade organic substances, and generate electrons. The electrons then flow through an external circuit and reach the catalyst-loaded cathode for oxygen reduction reactions (ORRs), through which electricity is generated [5]. MFCs have been

extensively studied for treating various types of organic wastes (e.g. municipal/industrial wastewater streams, landfill leachate) [9–17].

Methanol, as a widely used industrial precursor, is a common component in industrial waste stream [18,19]. It has been used in the production of diverse organic chemicals, such as formaldehyde, acetic acid and methyl tert-butyl ether (MTBE), and in biodiesel production. Due to the simple molecular structure and the high biodegradability, methanol is a carbon source suitable for microorganisms in biological nutrient removal (BNR) processes [20–23]. The toxicity threshold of methanol to certain groups of microorganisms can be as high as 1000 mg L⁻¹ (0.031 M) [24]. Methanol is also widely used as the fuel in direct methanol fuel cell (DMFC) since it can be easily stored and transported [25,26].

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Up to date, successful methanol treatment in MFCs has not been realized yet. There is only one study of treating methanol treatment in MFCs [27], in which methanol (10 mM) was added at the anode inoculation stage as the sole fuel source for bacteria in a two-chambered MFC, and anaerobic sludge obtained from a secondary anaerobic digester was used as inoculum. However, there was no appreciable power generation (voltage was ~ 10 mV with 470 Ω external resistance) even after acclimating for 320 h. This indicated that methanol is not able to act as the sole fuel source in MFCs. Co-digestion of methanol with other easily biodegradable organic compounds (e.g. fatty acid and carbohydrate) contained in wastewater could be a solution to increase the conversion of methanol to electricity in MFCs.

Platinum-based (Pt) cathodes are commonly used in both MFCs and DMFCs for its high oxygen reduction reaction (ORR) catalyzing capability on the cathode surface [5,26,28–32]. However, Pt catalyst could easily get poisoned by the accumulation of the intermediate products (e.g. CO_{ad}) from methanol oxidation reaction on the cathode surface, which diminish its catalytical capability and lower the power output [31–33]. Extensive studies with Pt based DMFCs have been carried out to alleviate the poisoning effects through cathode doping techniques (e.g. PtRu, PtFe, graphene-based nanoPt, tungsten carbide-based Pt) [33–39] or replacing Pt catalyst with other materials (e.g. gold, NiZr, RuSe, tungsten-based compounds and transition metal oxides) [26,40]. Only a few studies were conducted on the poisoning effects of chemicals (e.g. Cl^- , HSO_4^- , HPO_4^{2-} , HS^- and CO) on Pt-based cathodes [41–44]. These chemicals could severely deactivate the cathode catalytical sites for ORR in MFCs. Similarly, using Pt based MFCs to treat methanol could suffer the cathodic poisoning problem, and methanol could potentially poison the electrogenic bacteria on anode and affect power generation. Till now, the methanol poisoning effect to cathodic catalysts and electrogenic bacteria in MFCs has yet to be thoroughly studied. It is of great interest to develop novel cathodic catalysts, other than Pt catalyst, with high resistance towards methanol poisoning.

[*meso*-Tetrakis(4-methoxyphenyl)porphyrinato]cobalt(II) (CoTMPP) deposited on carbon and annealed at 800 $^\circ\text{C}$ was previously shown to be catalyzing the four-electron reduction of dioxygen (to water) [45]. The heat treatment forms many catalytic bis-cobalt centers. Annealed CoTMPP-based cathodes had the same current density as Pt cathodes treating glucose [32]. Our previous studies showed that poly([*meso*-tetrakis(2-thienyl)porphyrinato]cobalt(II)) (pCoTTP), a room-temperature electro-polymerized form of [*meso*-tetrakis(2-thienyl)porphyrinato]cobalt(II) (CoTTP), also exhibited good electrocatalytic activity for the four-electron reduction of oxygen [46]. In addition, this electrode had an excellent resistance to methanol poisoning compared to a traditional Pt/carbon electrode, which might be the result of the much lower potential of pCoTTP for ORR than for methanol oxidation [47]. The cobalt porphyrin structures in both CoTMPP and CoTTP are identical, and the two compounds vary merely in the nature of the side groups.

In terms of cost-effective cathode materials for utilization in MFCs treating methanol-containing waste streams, CoTTP could be a suitable precursor for the formation of heat-annealed electrocatalytic electrode materials. This study focused on the preparation of a cost-effective CoTTP cathode allowing high power generation of MFCs treating methanol. A traditional Pt cathode was used as a comparison. Specifically, three tasks are delineated in this study. First, the performance of CoTTP-based cathodes were determined in single chamber MFCs (SCMFCs) treating municipal wastewater containing methanol. Power generations, chemical oxygen demand (COD) degradation, and Coulombic efficiencies (CEs) were examined. Second, the concentration-dependent effects of methanol on cathode catalysis were determined. The electrochemical properties of cathodes were evaluated using linear sweep voltammetry (LSV)

and cathode open circuit potential (OCP). Third, the performance of CoTTP cathodes were studied at different CoTTP loadings.

2. Experimental

2.1. Single chamber microbial fuel cell (SCMFC)

Batch-mode single chamber MFCs (SCMFCs, volume: 130 mL) with air-cathodes were used as previously described [48]. The anodes were made of carbon cloth (non-wet proofing, Type-A, E-Tek, FL) with a dimension of 20 cm^2 (4×5 cm). Two types of cathodes, namely, Pt- and CoTTP-based cathodes (effective area: 5 cm^2) were examined. Powdered CoTTP (prepared as described previously [46]) was mixed with Vulcan XC-72 carbon (weight ratio of 1:9) and the mixture was then suspended in chloroform (320 mg/100 mL) whereby the porphyrin dissolved. The mixture was then dried by evaporating the chloroform solvent in a flask on a water bath. The dried-up material was then moved into a tubular vacuum oven at 800 $^\circ\text{C}$ for 2 h. The Pt cathode was fabricated as previously described [32], except that the air-facing side of both Pt and CoTTP cathodes were coated with four layers of polytetrafluoroethylene (PTFE) [29]. The Pt loading was ~ 0.5 mg cm^{-2} , and the CoTTP loadings were ~ 0.5 mg cm^{-2} and ~ 1.0 mg cm^{-2} , respectively. The external resistance of 550 Ω was applied to all SCMFCs.

2.2. SCMFC operation

The anodes were pre-inoculated for 2 months in municipal wastewater collected from the wastewater treatment facility at the University of Connecticut, and then put into the SCMFCs. The anode chamber was refilled with wastewater or wastewater–methanol mixtures at the end of each cycle when the voltage dropped below 0.05 V. Four methanol concentrations (0.005 M, 0.01 M, 0.02 M and 0.04 M) were examined. The low methanol concentrations (0.005 M) simulated the municipal wastewater, while the highest concentration (0.04 M) was the equivalent to the methanol content in the effluent of biodiesel waste glycerol fermentation [19]. Each methanol concentration was tested in duplicate (two cycles) except for 0.04 M methanol, which was tested in only one cycle (>200 h). All SCMFCs were operated at 30 $^\circ\text{C}$.

2.3. Methanol volatilization test

Because of the high volatility of methanol (bp = 64.7 $^\circ\text{C}$) and the long cycle durations, ranging from tens to hundreds of hours, methanol could evaporate through the sealed SCMFC anode chamber to atmosphere. This would cause the overestimation of the methanol degradation efficiency. To evaluate the possibility of methanol evaporation, a SCMFC was filled with distilled water containing 0.04 M methanol, and the methanol content was measured after 200 h using an Agilent 6890N gas chromatograph (GC) equipped with a fused silica capillary and a flame ionization detector (FID).

2.4. SCMFC performance analysis

The characteristics of wastewater and wastewater–methanol mixture in SCMFCs were measured at the beginning and the end of each cycle. The pH values of the chamber contents were measured using a portable pH meter (Thermo Fisher Scientific Orion 3 star) at the start and end of each cycle. Chemical oxygen demand (COD, mg L^{-1}) concentration was measured using HACH COD vials (20–1500 mg L^{-1} and 500–15,000 mg L^{-1}) and a DR 220 spectrophotometer (HACH, Loveland, CO) following the standard procedure. The COD degradation was determined by converting methanol concentration to equivalent COD. The possible remaining methanol

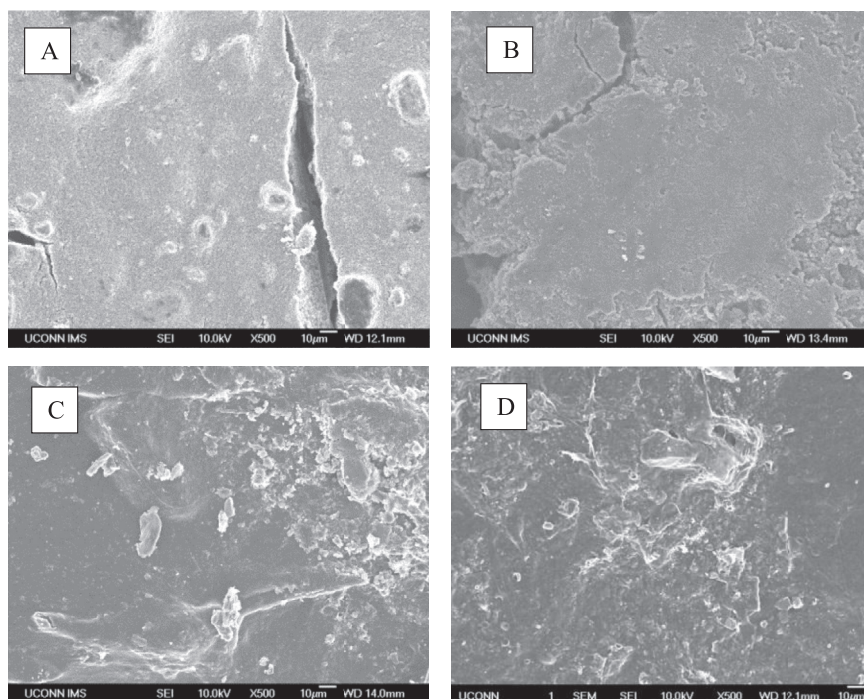


Fig. 1. The SEM images of cathodes in SCMFCs before and after 900 h of operation (A. Clean 0.5 mg cm^{-2} Pt loaded cathode; B. Clean 0.5 mg cm^{-2} CoTTP loaded cathode; C. 0.5 mg cm^{-2} Pt loaded cathode after 900 h operation; D. 0.5 mg cm^{-2} CoTTP loaded cathode after 900 h operation).

in effluent was examined using a gas chromatograph (GC). Prior to analysis, all liquid samples were filtered through a $0.2 \mu\text{m}$ pore size filter membrane. The voltage (V) over the external resistance was recorded every 2 h by a Keithly 2700 data logging system.

Linear sweep voltammetry (LSV) of cathodes was measured in a three-electrode configuration system using a potentiostat (Gamry P600) to evaluate the cathode electrochemical activities [17]. All the LSVs were operated in a low scan rate of 0.25 mV s^{-1} to avoid damage to the cathode [48]. The voltages were expressed vs SHE. The LSVs were conducted at the end of the cycle at each methanol concentration. The open circuit potential (OCP) of cathodes was measured using a potentiostat.

The power generations of SCMFCs were determined via polarization curves using a series of external resistances (R_{ext}) (48–2940 Ω), and a corresponding voltage (V) was acquired using a multimeter when the reading stabilized. The current density and power density were calculated according to $I = V * (A \times R_{\text{ext}})^{-1}$ and $P = V^2 * (A \times R_{\text{ext}})^{-1}$, respectively, where A is the effective area of the cathode. Coulombic efficiency (CE) was calculated for each cycle as previously described [49].

2.5. Cathode surface observation

The clean cathodes and the biofilm growth on cathodes catalyst after the test were observed using a Scanning electron microscopy (SEM) as previously described [23]. The contents of the CoTTP powder and Pt cathode were analyzed using the energy-dispersive X-ray spectroscopy (EDX).

3. Results and discussion

3.1. Surface properties of cathodes before and after operation

The Pt/carbon and CoTTP/carbon mixtures possessed a fine powder structure with discernible pores on the clean cathode surface (before the SCMFC tests) (Fig. 1A and B). After the SCMFCs

treating methanol for 900 h, biofilms fully grew on all cathodes tested (Fig. 1C and D). There was no clear difference between biofilms growing on the Pt cathodes and CoTTP cathodes, indicating that the catalyst type (and the presence of methanol in wastewater) did not affect biofilm growth on the cathodes.

The EDX profiles of the CoTTP powder and Pt cathode were compared (Fig. 2). Co and Pt elements were clearly located in EDX curves. The element S came from the thienyl groups in CoTTP (Fig. 2A) and the element F came from PTFE layer of the cathode (Fig. 2B).

3.2. Voltage generation trend of SCMFCs over 900 h of operation

During the 900 h of operational period, voltage generation did not decrease substantially in SCMFCs, with the maximum voltages ranging between 0.12 and 0.14 V (Fig. 3), demonstrating that the presence of methanol in the wastewater did not inhibit power generations. In addition, the cycle durations were prolonged with increasing methanol concentrations, with 25–30 h per cycle for wastewater and 70–250 h/cycle for wastewater containing 0.04 M methanol (Table 1). The main reason was that the COD concentration of anodic solution increased with methanol concentrations, and provided more substrates for the electrogenic bacteria.

It should also be noted that the ranking of the maximum voltages from SCMFCs changed when methanol concentrations increased. Specifically, at the beginning of the tests, no methanol was added to wastewater, all SCMFCs had similar maximum voltages (0.14 V) (Fig. 3). When methanol concentration increased, the maximum voltages generated of the CoTTP-based SCMFCs (0.12–0.13 V) became higher than that of Pt-based SCMFCs (0.09–0.12 V). This result indicated that CoTTP catalyst had higher tolerance to methanol than Pt cathodes.

3.3. Effects of methanol concentrations and cathode types on power generations of SCMFCs

Power generations were measured for SCMFCs treating the following typical influents: wastewater alone (Fig. 4A), wastewater

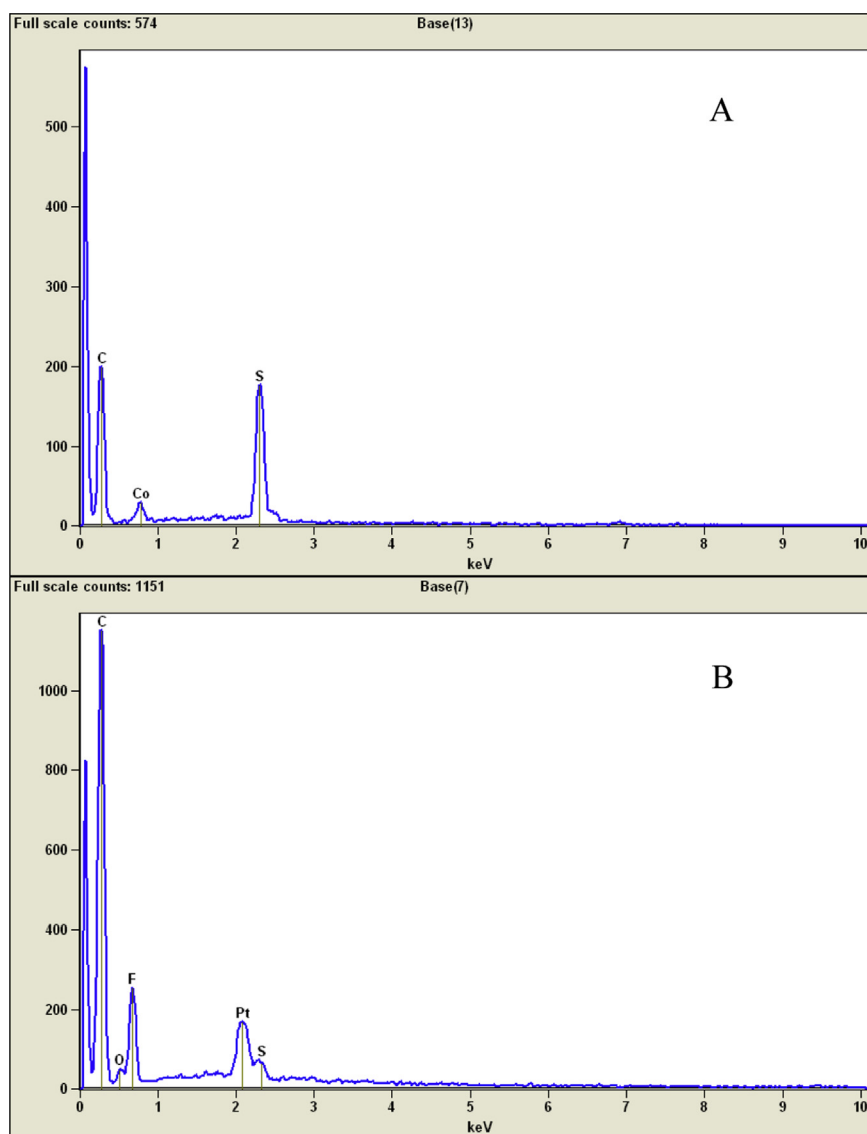


Fig. 2. The Energy-dispersive X-ray spectroscopy (EDX) of CoTPP powder prior to 800 °C pre-heating (A) and clean 0.5 mg cm⁻² Pt loading cathode (B).

containing 0.01 M methanol (Fig. 4B), wastewater containing 0.04 M methanol (Fig. 4C). When treating wastewater alone, the power generation of the Pt-based SCMFCs was much higher than that of SCMFCs with low CoTPP loading (0.5 mg cm⁻² loading) and slightly higher than that of SCMFCs with high CoTPP loading (1.0 mg cm⁻²) (Fig. 4A). When 0.01 M methanol being present, the power generation of Pt-based SCMFCs started dropping and was lower than that of SCMFCs with 1.0 mg cm⁻² loading CoTPP, but still

higher than that of SCMFCs with 0.5 mg cm⁻² loading CoTPP (Fig. 4B). When the methanol concentration was further increased to 0.04 M, the power generation of Pt-based SCMFCs dropped substantially, and was much lower than that of SCMFCs with the CoTPP electrode (at both 0.5 and 1.0 mg cm⁻² loadings, Fig. 4C). The variation of power generation of SCMFCs with different types of cathodic catalysts and different methanol concentrations indicated that methanol clearly inhibited Pt-cathodic activities, but only

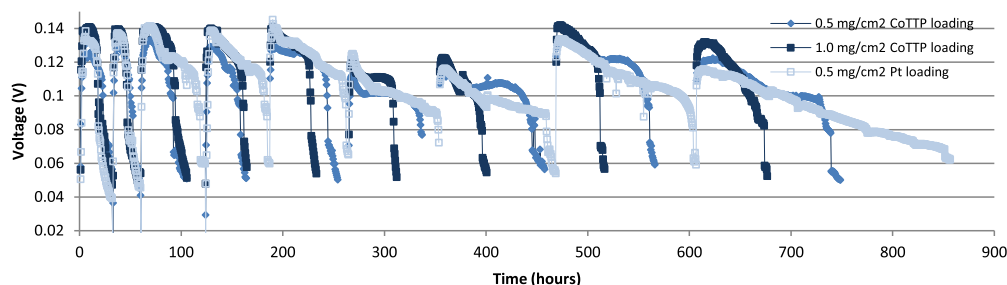


Fig. 3. Voltages generation trend of SCMFCs with CoTPP and Pt cathodes for 900 h.

Table 1
Cycle durations (hours) of SCMFCs at different methanol concentrations.^a

Cathodes	Wastewater alone	0.005 M methanol	0.01 M methanol	0.02 M methanol	0.04 M methanol
0.5 mg cm ⁻² CoTTP loading	29 ± 3	42.5 ± 2.5	69.5 ± 2.5	100 ± 3	142
1.0 mg cm ⁻² CoTTP loading	29 ± 2	42.5 ± 2.5	46 ± 1	47 ± 1	70
0.5 mg cm ⁻² Pt loading	25.5 ± 0.5	61.5 ± 1.5	83 ± 6	126 ± 12	250

^a Average values of two cycles under each condition.

slightly inhibited CoTTP cathodes, and CoTTP loadings affected the power generation of MFCs. Previously studies also found the methanol poisoning effect on Pt catalyst [33–35].

3.4. Effects of methanol concentrations and cathode types on COD/methanol removal and Coulombic efficiency

The effects of cathode types (Pt and CoTTP) and methanol concentrations (0–0.04 M) on COD degradation efficiencies of SCMFCs

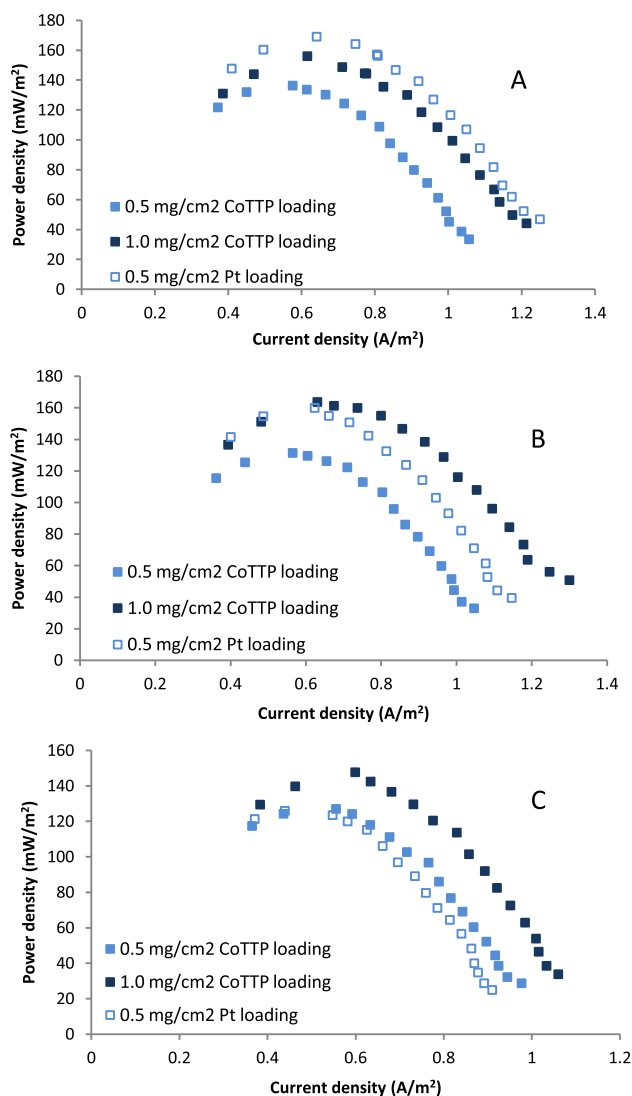


Fig. 4. Power generations of SCMFCs at different methanol concentrations. (A) Wastewater alone, (B) wastewater containing 0.01 M methanol, (C) wastewater containing 0.04 M methanol.

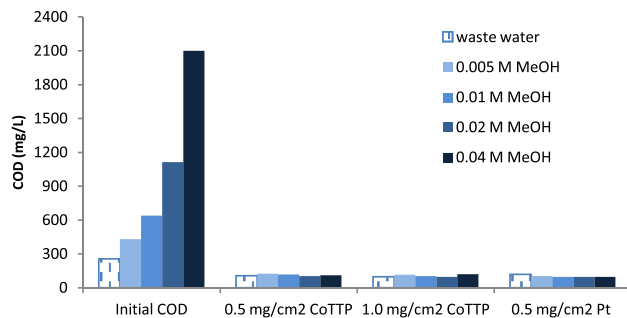


Fig. 5. Influent and effluent COD values of SCMFCs at different methanol concentrations.

were examined. The initial COD concentration varied from 220 mg L⁻¹ to 1110 mg L⁻¹ as an effect of the initial methanol concentrations, but the effluent COD was around 100 mg L⁻¹ for all SCMFCs (Fig. 5). This indicated that SCMFCs could thoroughly degrade municipal wastewater containing methanol (up to the tested concentration of 0.04 M). Most importantly, the COD degradation using the CoTTP-based cathode was not affected by the presence of methanol.

It should also be noted that the cycle durations of SCMFCs with CoTTP cathodes were much shorter than that of SCMFCs with Pt cathodes (as shown in Fig. 2, summarized in Table 1). The cycle duration of the lower loading CoTTP-based cathode SCMFCs (0.5 mg cm⁻² loading) were longer than those of high loading SCMFCs (1.0 mg cm⁻² loading). Short cycle duration could be an indication of faster degradation rate of methanol, implying that CoTTP catalyst enhanced the ORR rate on cathode as well as the overall biochemical reactions in SCMFCs [50].

The Coulombic efficiencies (CEs) were quite different for SCMFCs treating different methanol concentrations (0–0.04 M) (Fig. 6). Overall, all SCMFCs had low CE values (<11%) when methanol was present. This result proved that high COD removal efficiencies correspond to low CE values. This is consistent with previous studies and could be caused by the over-growth of anaerobic bacteria rather than electricity generation [51]. When treating wastewater alone, all SCMFCs had the high CEs (11–16%), with the highest CE value obtained from high loading CoTTP SCMFC (1.0 mg cm⁻²). When methanol was added to wastewater, the CEs started to decline in all SCMFCs, and were lower than 6% at 0.04 M methanol. Although CoTTP catalysts provided a faster ORR and a high methanol degradation rate, they decreased the CEs compared with Pt cathodes, and higher CoTTP loadings had lower CEs than lower CoTTP loadings (Fig. 6). The CE values indicate the capability of MFC to convert methanol into electricity [50]. Considering the high removal of methanol in SCMFCs (as shown in Fig. 5), the low CEs revealed that methanol was degraded via other pathways

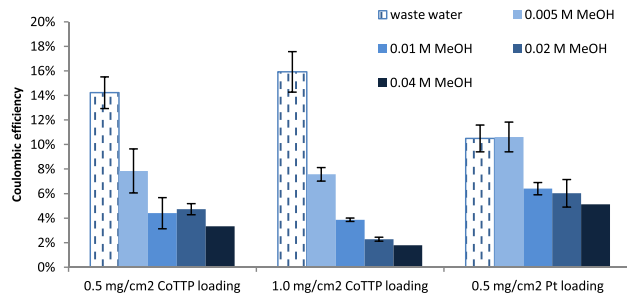


Fig. 6. Coulombic efficiencies (CE) of SCMFCs at different methanol concentrations.

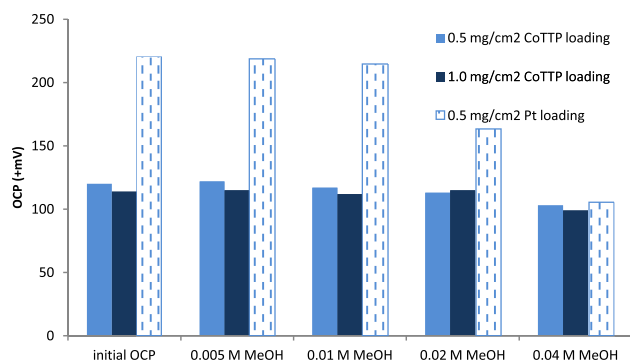


Fig. 7. Cathode open circuit potentials (OCVs) variations of the three SCMFCs at different methanol concentrations.

rather than electrochemical pathway. This further indicated that although CoTTP had higher tolerance to methanol than Pt cathodes, it was not as effective as Pt cathodes in terms of converting methanol to electricity.

Methanol removal pathways in SCMFCs could involve three pathways: electrochemical conversion, anaerobic bio-degradation, and volatilization. Methanol has low volatility and high solubility [20], and the methanol volatilization tests in SCMFCs showed no detectable methanol loss over a 200 h period (data not shown). Thus, methanol volatilization in SCMFCs could be ignored. Biodegradation is responsible for most methanol removal and microorganisms play a dominant role in bio-degradation of methanol [20]. Given the anaerobic environment of the SCMFCs in this study, anaerobic bacteria in the anode chamber are expected to degrade most methanol. This was further evidenced by the low CEs (Fig. 6) and high COD removal efficiencies (Fig. 5).

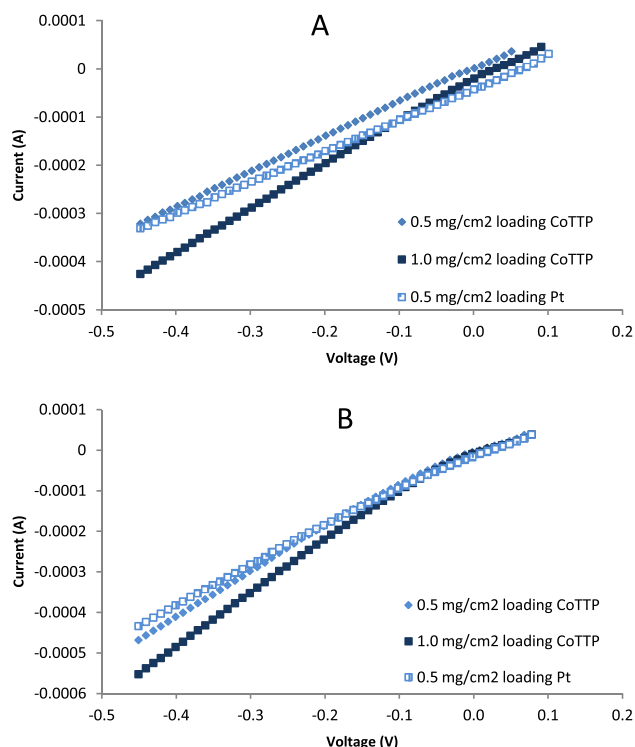


Fig. 8. Typical linear sweep voltammeteries (LSVs) of SCMFCs with different cathodes treating wastewater (A. Before methanol treatment; B. After methanol treatment).

3.5. Methanol poisoning effects on Pt based cathodes

The cathodes OCPs were recorded during the operational period to examine the effects of methanol concentrations on the cathodes. There was no clear difference between the OCPs of the clean CoTTP cathodes ($\sim +120$ mV for 0.5 mg cm^{-2} loading, $\sim +115$ mV for 1.0 mg cm^{-2} loading), but the OCP of the clean Pt cathode ($\sim +220$ mV) was almost twice higher than CoTTP cathodes (Fig. 7). The Pt cathodes exhibited relatively stable OCPs at low methanol concentrations (0.005 M and 0.01 M), dropped to $\sim +163$ mV at higher methanol concentration (0.02 M), and further dropped to $\sim +105$ mV at the highest methanol concentration (0.04 M). In contrast, CoTTP cathodes kept the stable OCPs at all methanol concentrations tested, and were $+99$ to $+115$ mV at the highest methanol concentration (0.04 M). This indicated that methanol started to have significant poisoning impact on Pt cathode after reaching certain concentration (0.02 M) but the poisoning impact to CoTTP cathodes was minimal.

The methanol poisoning effects on different cathodes were compared using multiple LSV measurements, with a typical profile demonstrated in Fig. 8. Prior to treating methanol, the higher loading CoTTP cathode (1.0 mg cm^{-2}) had the highest electrocatalytic activity when the bias potential was -0.45 V to -0.15 V , while the lower loading CoTTP cathode (0.5 mg cm^{-2}) had the lowest electrocatalytic activity at the entire bias potential range (Fig. 8A). The electrocatalytic activity of Pt cathode was slightly higher than that of 1.0 mg cm^{-2} CoTTP cathode at lower bias potential range (-0.15 V to 0 V), but was lower at higher bias potential. However, after treating methanol (0.005 – 0.04 M , over 900 h , Fig. 3), the Pt cathode exhibited the lowest electrocatalytic activity among the three cathodes while the 1.0 mg cm^{-2} CoTTP cathode still had the highest electrocatalytic activity (Fig. 8B). It should be noted that the absolute values of the overall currents after methanol addition (Fig. 8B) were slightly higher than those before methanol addition (Fig. 8A). This did not mean that methanol addition increased cathode activity; instead, the methanol addition increased the conductivity of feeding solution, which led to higher currents of all cathodes. Overall, the electrocatalytic activity results showed that CoTTP cathodes exhibited a higher tolerance towards methanol poisoning than Pt cathodes.

3.6. Mechanisms of CoTTP cathodes tolerating methanol

Various products or intermediates could be formed during methanol oxidation [52]. Carbon monoxide (CO) generated from methanol oxidation could be bonded to the Pt catalyst and cause irreversible damage to the catalytic activity [26], explaining the decrease of power generations in the Pt based cathode SCMFCs.

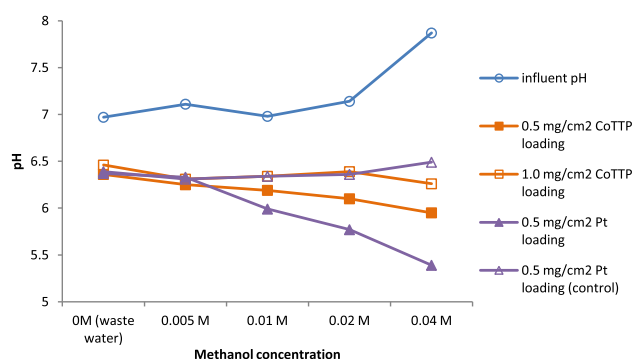
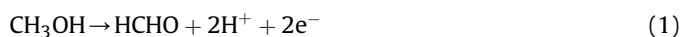


Fig. 9. pH variations of SCMFCs with Pt cathodes and CoTTP cathodes at different methanol concentrations.

Methanol oxidation may generate formic acid (Equations (1)–(3)) [26], that inevitably decrease the pH of the SCMFC anode solution (Fig. 9). The pH values were recorded at the start and end of each cycle for all SCMFCs including a control SCMFC (0.5 mg cm⁻² Pt cathode) treating wastewater alone. With the increase in methanol concentration, the SCMFCs with Pt cathode experienced a much sharper pH drop than those with CoTTP cathodes, while the control SCMFCs containing no methanol maintained a relatively stable pH. There could be two reasons. First, the CoTTP structure provided a much lower ORR potential than methanol oxidation, which prevented it from methanol oxidation and subsequent poisoning. Or the unique porphyrin structure of the annealed CoTTP is inert to any poisoning (e.g. Co_{ad} poisoning) [53]. Instead, more oxygen or hydroxyl radicals (OH•) adsorptions on the catalyst surface would take place [54], which explains the high electrocatalytic activity on the CoTTP cathodes (Fig. 8). Higher CoTTP loadings greatly increased the power generations compared with low CoTTP loadings, due to a more active electrochemical catalysis.



3.7. Significance for SCMFCs with methanol tolerant electrodes treating wastewater

Novel cost-effective Pt-free CoTTP cathodes with high methanol tolerance were developed for co-digestion of methanol with wastewater in SCMFCs. Although methanol is an easily biodegradable compound in soil and wastewater under a wide range of environmental conditions [55], the breakthrough of this study was to convert methanol into electricity in SCMFCs, which yields profound significance for sustainably treating diverse waste streams containing methanol. CoTTP cathode based SCMFCs achieved 100% methanol removal efficiency at the methanol concentration range of 0.005 M up to 0.04 M. All SCMFCs in this study were able to partly convert methanol into electricity despite of low CE values. Even though the addition of methanol to wastewater in SCMFCs did not increase power generation, at least it did not decrease the power generation of SCMFCs with annealed CoTTP cathodes, which was the major breakthrough for applying MFCs treating methanol. The results implied that SCMFCs, with simple configuration and high power generation, could be applied as the follow-up process to treat the effluent of glycerol waste stream fermentation (containing methanol) [19]. In addition, compared with Pt based cathodes, the cost-effective CoTTP based cathodes exhibited faster methanol removal rate and higher power generation, and could be used as a substitute for costly Pt cathodes in MFCs.

4. Conclusions

Novel CoTTP cathodes capable of tolerating methanol poisoning were, for the first time, developed in batch-mode SCMFCs treating wastewater and methanol at different concentrations (0.005 up to 0.04 M) for over 900 h. Four conclusions can be drawn:

First, the SCMFCs with CoTTP cathodes had shorter cycle duration than those with Pt cathodes. The power generation of the SCMFCs with Pt cathodes gradually weakened over time, while the power generation of the SCMFCs with CoTTP cathodes was relatively stable.

Second, methanol was completely removed from the waste streams in SCMFCs though anaerobic degradation was the main

degradation pathway. The CEs of the SCMFCs with Pt cathodes were higher than those with CoTTP cathodes.

Third, the cathodic OCP measurement indicated that higher methanol concentrations (>0.02 M) had deleterious effects on Pt cathodes but did not inhibit CoTTP cathodes. Higher CoTTP loading exhibited similar OCP values compared to lower one. The power curves and cathodic LSVs showed that the electrocatalytic activity of Pt cathodes dropped with the presence of methanol, while the CoTTP cathodes maintained good electrocatalytic activity.

Fourth, CoTTP cathodes successfully treated methanol up to 0.04 M in wastewater, and exhibited higher tolerance towards methanol than Pt cathodes. CoTTP catalyst is a promising substitute for Pt catalyst to treat methanol in SCMFCs.

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